

METALLO-ORGANIC COMPOUNDS CONTAINING METAL-NITROGEN BONDS.

D.C. Bradley, I.M. Thomas and E.G. Torrible

Chemistry Department, The University of Western Ontario,
London, Ontario, Canada.

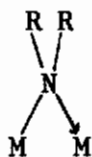
ABSTRACT

By means of reactions involving transition metal chlorides MCl_x and lithium dialkylamides a number of new dialkylamino-derivatives of titanium, zirconium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten have been prepared. Aminolysis of some of these compounds involved considerable steric effects due to shielding of the metal atom. In the case of quinque-valent niobium and tantalum the steric effect precluded the formation of pentakis-derivatives except with dimethylamino-, N-methyl-n-butylamino-, and piperidino-groups. With higher dialkylamines the products were $Nb(NR_2)_4$ and $RN-Ta(NR_2)_3$. Studies on the reactions of dialkylamino-titanium compounds with primary amines showed that polymeric compounds may be obtained.

Report Documentation Page			Form Approved OMB No. 0704-0188		
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE 1962		2. REPORT TYPE		3. DATES COVERED 00-00-1962 to 00-00-1962	
4. TITLE AND SUBTITLE Metallo-Organic Compounds Containing Metal-Nitrogen Bonds			5a. CONTRACT NUMBER		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S)			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Paul V. Galvin Library, 35 W. 33rd Street, Chicago, IL, 60616			8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSOR/MONITOR'S ACRONYM(S)		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S)		
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT By means of reactions involving transition metal chlorides MCl_x and lithium dialkylamides a number of new dialkylamino-derivatives of titanium, zirconium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten have been prepared. Aminolysis of some of these compounds involved considerable steric effects due to shielding of the metal atom. In the case of quinquevalent niobium and tantalum the steric effect precluded the formation of pentakis-derivatives except with dimethylamino-, N-methyl-<i>tert</i>-butylamino-, and piperidino-groups. With higher dialkylamines the products were Nb(NR₂)₃ and RN=Ta(NR₂)₃. Studies on the reactions of dialkylamino-titanium compounds with primary amines showed that polymeric compounds may be obtained.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 10	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

INTRODUCTION

The dialkylamino- compounds of the transition metals were of special interest since they bridge the gap between the relatively stable metal alkoxides and the generally unstable metal alkyls. In addition there was the possibility that metal-nitrogen polymers would be formed, either by coordination-polymerization (I) in which the lone-pair of electrons on the nitrogen forms an inter-molecular coordinate bond, or by using the bifunctional primary amine as in (II).



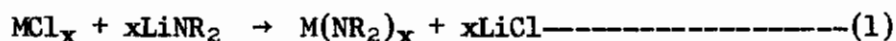
(I)



(II)

In the case of the primary amino-derivatives there was the further possibility that coordination-polymerization would also take place. There were also some factors which might operate against polymerization. Thus in the dialkylamino-derivatives the intermolecular bond (I) might be prevented by steric effects or by "intramolecular coordination" involving σ - π bonds $M \leftarrow NR_2$. In the case of primary amino-derivatives there was the further possibility that only one of the hydrogens of the NH_2 - group would be replaceable by metal and this would prevent polymerization by mechanism (II). Prior to 1959 the only binary dialkylamino-compound of a transition metal or actinide element reported was the tetrakis-(diethylamino)-uranium (IV) obtained by Gilman and coworkers¹ from the reaction involving uranium tetrachloride and lithium diethylamide. Dermer and Fernelius² prepared $Ti[N(C_6H_5)_2]_4$ by treating titanium tetrachloride with sodium diphenylamide.

We have shown that the lithium dialkylamide- metal chloride reaction (I) is suitable for the synthesis of numerous dialkylamino-derivatives of titanium, zirconium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten.



Most of the dialkylamino-derivatives may be distilled under reduced pressure although in some cases [e.g. Nb(V), Ta(V) compounds] interesting thermal decomposition occurs. The aliphatic dialkylamino- compounds were readily hydrolysed or alcoholysed but arylamino-derivatives were relatively more stable. Some interesting steric effects were observed in the dialkylamino- compounds whilst in the primary amino- compounds a number of polymeric derivatives were obtained.

Titanium and Zirconium Compounds

1. Dialkylamino-, and other secondary amino-derivatives.

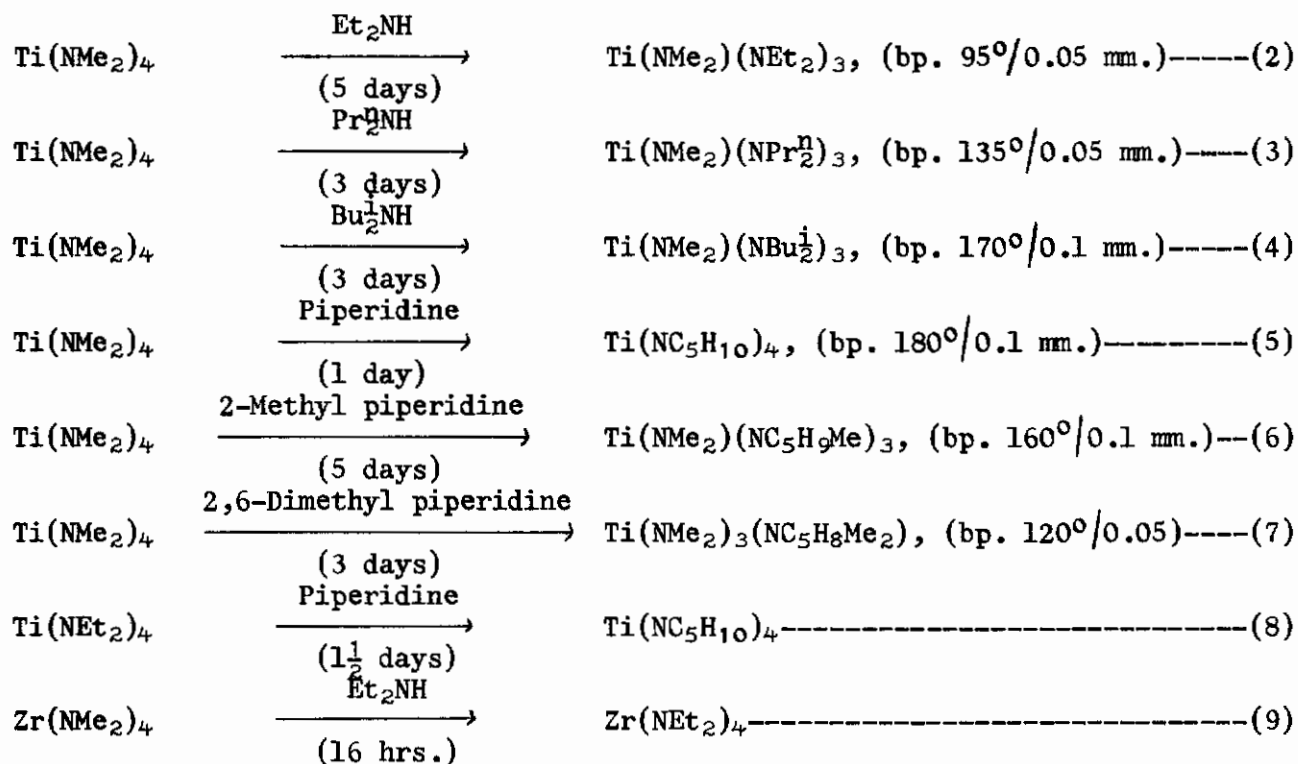
Some data on tetrakis-(dialkylamino)-titanium and zirconium compounds³ are presented in Table 1.

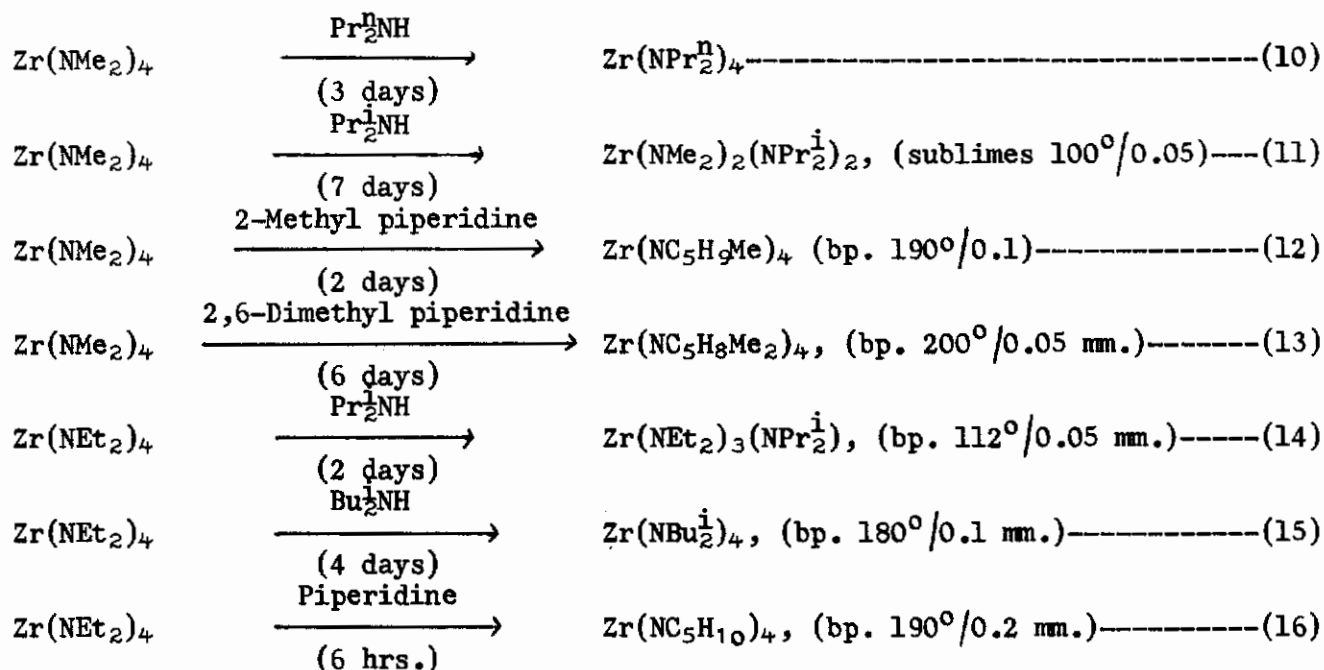
Table 1

<u>Compound</u>	<u>Appearance</u>	<u>Boiling point (°C mm.Hg.)</u>
$\text{Ti}(\text{NMe}_2)_4$	Yellow liquid	50/0.05
$\text{Ti}(\text{NEt}_2)_4$	Orange liquid	112/0.1
$\text{Ti}(\text{NPr}_2)_4$	Red liquid	150/0.1
$\text{Ti}(\text{NBu}_2)_4$	Red liquid	170/0.1
$\text{Zr}(\text{NMe}_2)_4$	White solid (mp. 70°)	80/0.05
$\text{Zr}(\text{NEt}_2)_4$	Green liquid	120/0.1
$\text{Zr}(\text{NPr}_2)_4$	Green liquid	165/0.1
$\text{Zr}(\text{NBu}_2)_4$	Green solid	180/0.1 (sublimes)

Some tetrakis-(dialkylamino)-titanium and -zirconium compounds

Only in the case of $\text{Zr}(\text{NMe}_2)_4$ was there any evidence of polymerization at the boiling point of benzene and it is noteworthy that the compound is significantly less volatile than the corresponding titanium derivative. From a consideration of the steric effects demonstrated in the aminolysis of these tetrakis-(dialkylamino)-derivatives it was deduced that the absence of polymerization was a consequence of the powerful shielding of the central atom by the dialkylamino- groups. In the aminolysis reactions an excess of a higher boiling amine was added to the tetrakis-(dialkylamino)-derivative and the liberated lower boiling amine was fractionated off until it appeared that the reaction was complete. The extent of these reactions is shown in the following equations.

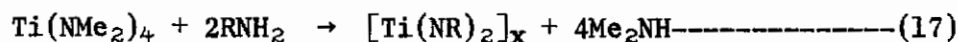




The above reactions are readily interpreted as controlled by steric factors. For example in the case of titanium compounds it is clear that the dimethylamino- groups in $\text{Ti(NMe}_2)_4$ are equally replaced by diethylamino-, di-n-propylamino-, or di-iso-butylamino- groups although the experimental conditions were not strictly comparable. However, when di-iso-propylamine was used only a small amount of $\text{Ti(NMe}_2)_3(\text{NPr}_2^{\text{H}})$ was formed in a reaction lasting 6 days. Even more striking was the behaviour of piperidine, 2-methyl piperidine, and 2,6-dimethyl piperidine. In the reaction with piperidine all of the dimethylamino-groups were replaced because piperidine exerts a smaller steric effect than the di-n-alkylamino- groups (excepting $\text{Me}_2\text{N-}$). When 2-methyl piperidine was used substitution was limited to the formation of $\text{Ti(NMe}_2)(\text{NC}_5\text{H}_9\text{Me})_3$ whilst with 2,6-dimethyl piperidine steric hindrance to substitution was so powerful that only one dimethylamino- group could be replaced. Nevertheless, it was evident that the steric effect of di-iso-propylamine was greater than that of 2,6-dimethyl piperidine. The behaviour of tetrakis-(dimethylamino)- zirconium was also in accordance with steric control of substitution. It would be predicted that the zirconium atom being larger than titanium would cause $\text{Zr(NMe}_2)_4$ to be more prone to nucleophilic reagents than $\text{Ti(NMe}_2)_4$. The veracity of this prediction was well established by the fact that complete substitution of dimethylamino- groups was achieved by $\text{Et}_2\text{N-}$, $\text{Pr}_2^{\text{H}}\text{N-}$, and $\text{Bu}_2^{\text{H}}\text{N-}$ groups in the case of zirconium in contrast to trisubstitution in the case of titanium. The complete substitution of dimethylamino- groups attached to zirconium by piperidine, 2-methyl piperidine, or 2,6-dimethyl piperidine emphasizes the importance of steric effects in these reactions. Only in the reaction of di-iso-propylamine with $\text{Zr(NMe}_2)_4$ which was restricted to disubstitution was there evidence of steric hindrance to substitution of tetrakis-(dimethylamino)-zirconium. On the other hand it would be expected that the greater steric effect of diethylamino- groups would lead to greater steric hindrance to substitution of $\text{Zr(NEt}_2)_4$. This was strikingly proved in the reaction with di-iso-propylamine which was confined to mono-substitution.

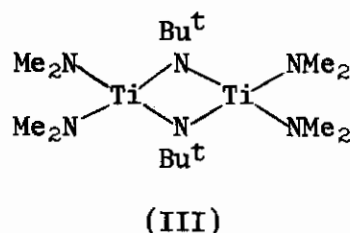
2. Derivatives of Primary amines.

When either $\text{Ti}(\text{NMe}_2)_4$ or $\text{Ti}(\text{NEt}_2)_4$ were treated with excess of the primary amine RNH_2 , where $\text{R} = \text{Pr}^n, \text{Pr}^i, \text{Bu}^n, \text{Bu}^i, \text{Bu}^s$, or cyclohexyl, a coloured solid approximating to the limiting formula $\text{Ti}(\text{NR})_2$ was formed. The colours ranged from orange through red to brown and the compounds were practically insoluble and non-volatile. These properties suggested that the compounds were highly polymeric due to metal-nitrogen bridges (II). It is clear that the primary amines are behaving as bifunctional reactants in the aminolysis:-

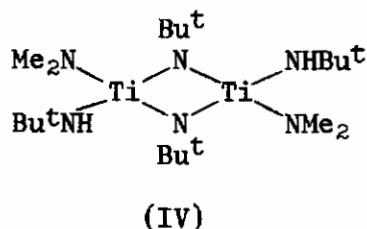


The primary amino-derivatives were all readily hydrolysed or alcoholysed.

When $\text{Ti}(\text{NMe}_2)_4$ was treated with excess tertiary butylamine only disubstitution occurred with the formation of the dimer $\text{Ti}_2(\text{NMe}_2)_4(\text{NBu}^t)_4$ which probably has the formula (III):-



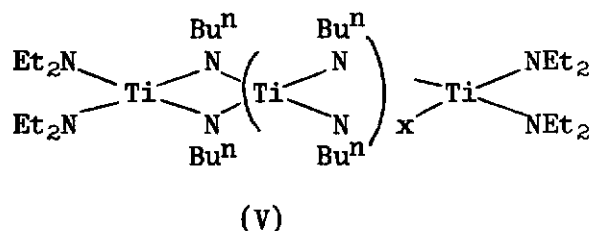
Once again it appeared that steric factors controlled the extent of the reaction. Prolonged treatment of (III) with excess of tertiary butylamine failed to produce any higher polymers although some replacement of dimethylamino-groups took place. Instead the volatile (sublimes $140-160^\circ/0.1 \text{ mm.}$) deep red solid dimer $\text{Ti}_2(\text{NMe}_2)_2(\text{NBu}^t)_2(\text{NHBu}^t)_2$ was obtained which may well have structure (IV)



In the reactions involving $\text{Ti}(\text{NEt}_2)_4$ and n -butylamine it was possible to isolate a number of soluble polymers of the general formula $\text{Ti}_n(\text{NBu}^n)_{2n-2}(\text{NEt}_2)_4$.



It is believed that these compounds are polymers involving tetrahedrally 4-coordinated titanium with terminal Et_2N - groups acting as chain stoppers as in (V)



These products were dark red non-volatile solids and polymers containing 6, 14, 16 and ca 100 titanium atoms per molecule were obtained.

A significant result was obtained from the reaction involving $\text{Ti}(\text{NMe}_2)_4$ and aniline. A black microcrystalline non-volatile solid corresponding in analysis to $\text{Ti}(\text{NC}_6\text{H}_5)_2$ remained after drying at $215^\circ/0.1$ mm. It was most interesting to find that this compound was noticeably less readily hydrolysed than any of the aliphatic primary amino-derivatives.

3. Tris-(diethylamino)-titanium (III).

From the reaction involving titanium trichloride and lithium diethylamide a brown liquid was obtained. From the analysis it was deduced that the compound was substantially the tervalent titanium derivative $\text{Ti}(\text{NEt}_2)_3$ containing some coordinated amine. When heated under reduced pressure the compound disproportionated to give tetrakis-(diethylamino)-titanium (IV) and left a non-volatile residue containing lower valency compounds of titanium.

Vanadium, Niobium and Tantalum Compounds

1. Vanadium Compounds.

Vanadium tetrachloride reacted with lithium dialkylamides to form tetrakis-(dialkylamino)-vanadium (IV) derivatives⁴. For example, $\text{V}(\text{NMe}_2)_4$ was obtained as a green solid (mp. 40° ; bp. $65^\circ/1.0$ mm.) and $\text{V}(\text{NEt}_2)_4$ was a dark green liquid (bp. $110^\circ/0.05$ mm.). Alcoholysis of the tetrakis-(dialkylamino)-vanadium derivatives afforded the vanadium tetraalkoxides.

Vanadium trichloride reacted with lithium diethylamide to form a dark brown liquid which was substantially tris-(diethylamino)-vanadium (III) with some coordinated diethylamine. This product resembled the corresponding titanium compound by undergoing disproportionation when heated in vacuo.

2. Niobium Compounds.

Studies of the reactions of niobium pentachloride with lithium dialkylamides led to some interesting results⁵. In the case of lithium dimethylamide the product was substantially pentakis-(dimethylamino)-niobium (V) with <10% of quadrivalent niobium present. The pure $\text{Nb}(\text{NMe}_2)_5$ was isolated by vacuum sublimation. With the higher dialkylamides the amount of quadrivalent niobium in the crude products increased steadily with length of the alkyl chain (i.e. Et, 69%; Pr^n , 85%; Bu^n , 91% reduction). In each case the tetrakis-(dialkylamino)-niobium (IV) compound was obtained by vacuum distillation. Some data on niobium compounds are given in Table 2.

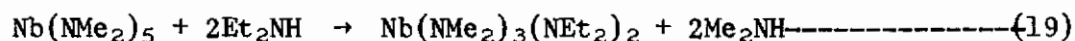
Table 2

<u>Compound</u>	<u>Appearance</u>	<u>Boiling point</u> (° C/mm.Hg)
Nb(NMe ₂) ₅	Brown solid	sublimes 100/0.1
Nb(NMeBu ⁿ) ₅	Red liquid	decomp. 150/0.1
Nb(NC ₅ H ₁₀) ₅	Yellow crystals	decomp. 170/0.1
Nb(NEt ₂) ₄	Brown liquid	120/0.1
Nb(NPr ⁿ) ₄	Red liquid	155/0.1
Nb(NBu ⁿ) ₄	Red liquid	175/0.1
Nb(NMeBu ⁿ) ₄	Red liquid	150/0.1
Nb(NC ₅ H ₁₀) ₄	Brown liquid	decomp. 170/0.1

Some Alkylamino-niobium Compounds.

We have interpreted the breakdown of pentakis-(dialkylamino)-niobium (V) compounds as being caused by steric compression within the molecule. Obviously the intramolecular compression will become more severe as the size of the di-n-alkylamino- group is increased. This is in accord with the increasing percentage of Nb(IV) found in the initial products from the NbCl₅-LiNR₂ reactions. This view is also supported by the additional facts that pentakis-derivatives were also obtained with N-methyl-n-butylamino- and piperidino- groups. Our work on titanium and zirconium compounds showed very clearly that the steric effect of the piperidino- group was significantly less than that of the diethylamino- and higher di-n-alkylamino- groups. Moreover, there can hardly be any doubt that the steric effect of the MeBuⁿN- group must be less than that for diethylamino- groups because the methyl group being small allows the n-butyl group to bend away from the centre of the Nb(NMeBuⁿ)₅ molecule.

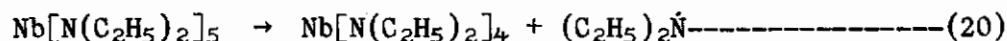
Further evidence for the existence of powerful steric effects was forthcoming from some reactions involving Nb(NMe₂)₅ and diethylamine. In one case the reactants were maintained at the boiling point of diethylamine for 2 hours and the liberated dimethylamine was fractionated off. No reduction of niobium occurred but aminolysis was restricted to disubstitution.



In another experiment continued for 9 days the replacement of dimethylamino- groups was still incomplete and about 30% reduction of niobium occurred. Distillation of the product gave the quadrivalent compound Nb(NMe₂)(NEt₂)₃ as a red liquid (bp. 120°/0.1 mm.). Evidently the niobium can accommodate three dimethylamino- groups and two diethylamino- groups but the introduction of the third or fourth diethylamino- groups leads to instability.

3. Thermal decomposition of pentakis-(dialkylamino)-niobium compounds.

The formation of tetrakis-(dialkylamino)-niobium (IV) compounds by thermolysis of the pentakis-(dialkylamino)-niobium (V) is extremely interesting and raises the question of mechanisms. Although the mechanism of the thermolysis has not yet been studied some useful observations may be made. Thus it was noticed that secondary amine was also liberated in the reaction and this suggests that the dialkylamino- radical is involved in hydrogen abstraction. The following equations suggest possible mechanisms for the thermolysis.



An interesting feature of the thermolysis of $\text{Nb}(\text{NMeBu}^n)_5$ was the formation of $\text{Bu}^n\text{N}=\text{Nb}(\text{NMeBu}^n)_3$ in addition to $\text{Nb}(\text{NMeBu}^n)_4$. This was the only case in which the quinquevalent $\text{RN}=\text{Nb}(\text{NRR}')_3$ was found because there was no evidence for the formation of such compounds in the thermolysis of the dialkylamino-derivatives.

4. Tantalum Compounds.

The reactions of tantalum pentachloride with various lithium dialkylamides LiX , where $\text{X} = \text{NMe}_2, \text{NEt}_2, \text{NPr}_2^n, \text{NMeBu}^n$ and NC_5H_{10} , were studied. From these reactions the corresponding pentakis-derivatives were obtained, in contrast to the behaviour of niobium pentachloride. However, only the pentakis-dimethylamino-derivative $\text{Ta}(\text{NMe}_2)_5$ could be sublimed without decomposition and this calls to mind the behaviour of $\text{Nb}(\text{NMe}_2)_5$. When the higher pentakis-(dialkylamino)-compounds of tantalum were heated in vacuo thermolysis took place with the formation of substantially the interesting quinquevalent compounds $\text{RN}=\text{Ta}(\text{NR}_2)_3$ together with some tetrakis-(dialkylamino)-tantalum (IV). Some data on the tantalum compounds are presented in Table 3.

Table 3

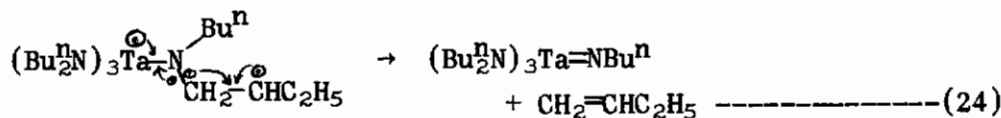
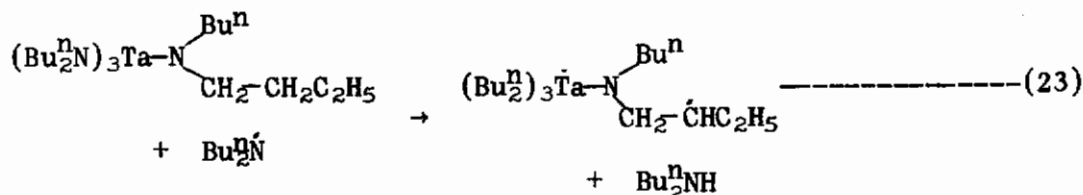
<u>Compound</u>	<u>Appearance</u>	<u>Boiling point</u> ($^{\circ}\text{C}/\text{mm.Hg}$)
$\text{Ta}(\text{NMe}_2)_5$	Yellow crystals	sublimes 100/0.1
$\text{EtN}=\text{Ta}(\text{NEt}_2)_3$	Yellow liquid	120/0.1
$\text{Pr}^n\text{N}=\text{Ta}(\text{NPr}_2^n)_3$	Orange liquid	150/0.1
$\text{Bu}^n\text{N}=\text{Ta}(\text{NBu}_2^u)_3$	Yellow liquid	180/0.1
$\text{Ta}(\text{NC}_5\text{H}_{10})_5$	Yellow solid	-
$\text{Ta}(\text{NMeBu}^n)_5$	Orange liquid	decomp. 160/0.1
$\text{Bu}^n\text{N}=\text{Ta}(\text{NMeBu}^n)_3$	Orange liquid	150-155/0.1
$\text{Ta}(\text{NMeBu}^n)_4$	Red liquid	155-180/0.1

Some Alkylamino-compounds of Tantalum.

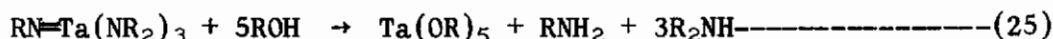
The detailed mechanism of the formation of the quinquevalent derivatives $\text{RN}=\text{Ta}(\text{NR}_2)_3$ is as yet obscure but from product analysis it appears that secondary amine and olefin are also produced in the thermolysis of $\text{Ta}(\text{NR}_2)_5$ compounds. We suggest as a tentative explanation that the pentakis-derivative dissociates to the tetrakis-derivative and a dialkylamino radical.



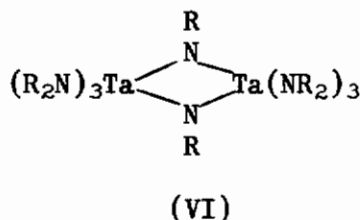
Further it is suggested that the quadrivalent tantalum compound is so unstable that it reacts with the radical before the latter becomes "free". A possible sequence would be hydrogen abstraction by the radical followed by the elimination of olefin.



The thermolysis of $\text{Ta}(\text{NMeBu}^n)_5$ was of added interest because of the choice of alkyl groups attached to the nitrogen. The formation of $\text{Ta}(\text{NMeBu}^n)_4$ and $\text{Bu}^n\text{N}=\text{Ta}(\text{NMeBu}^n)_3$ but not $\text{MeN}=\text{Ta}(\text{NMeBu}^n)_3$ suggests that a methyl group in $\text{Ta}(\text{NMeBu}^n)_4$ is preferentially attacked by the N-methyl-n-butylamino-radical. It is pertinent to examine the evidence on which the formula for the $\text{RN}=\text{Ta}(\text{NR}_2)_3$ derivatives is based. Firstly there is the analytical data for tantalum and nitrogen. However, the analytical figures for $\text{RN}=\text{Ta}(\text{NR}_2)_3$ are fairly near to those for $\text{Ta}(\text{NR}_2)_4$. The second factor is the determination of the average valency of the tantalum by a chemical method. This ruled out the quadrivalent formula $\text{Ta}(\text{NR}_2)_4$. The third and decisive piece of evidence was forthcoming from the identification of the primary amine RNH_2 in addition to the secondary amine among the products of alcoholysis.



However, there remains the possibility that the compound is the dimer $\text{Ta}_2(\text{NR})_2(\text{NR}_2)_6$ with a double primary amino-bridge as in (VI).



The dimeric structure (VI) was ruled out by the volatility of the compounds which were close to the volatilities of the monomeric tetrakis-(dialkyl-amino)-niobium (IV) compounds. Consequently we assign the monomeric formula $\text{RN}=\text{Ta}(\text{NR}_2)_3$ which contains the metal-nitrogen π -bond.

Chromium, Molybdenum and Tungsten Compounds.

When chromium trichloride was treated with lithium diethylamide a small yield of tris-(diethylamino)-chromium (III) was ultimately obtained as a volatile (bp. $90^\circ/0.1$ mm.) green liquid.

From the reaction involving molybdenum pentachloride and lithium diethylamide a very small yield of substantially pure tetrakis-(diethylamino)-molybdenum (IV) was obtained as a volatile (bp. $110^\circ/0.1$ mm.) violet liquid.

From molybdenum trichloride an impure tris-(diethylamino)-molybdenum (III) was obtained as a non-volatile brown gum.

When tungsten hexachloride was allowed to react with lithium diethylamide some tetrakis-(diethylamino)-tungsten (IV) was obtained as a volatile (bp. 120°/0.1 mm.) red liquid. All of these chromium, molybdenum and tungsten compounds were readily hydrolysed.

References

- ¹ Jones, R.G., Karmas, G., Martin, G.A., and Gilman, H., J.Amer.Chem.Soc., 78, 4285 (1956).
- ² Dermer, O.C., and Fernelius, W.C., Z.anorg.Chem., 221, 83 (1953).
- ³ Bradley, D.C., and Thomas, I.M., J.Chem.Soc., 3857 (1960).
- ⁴ Thomas, I.M., Can.J.Chem., 39, 1386 (1961).
- ⁵ Bradley, D.C., and Thomas, I.M., Can.J.Chem., (1962), In the press.
- ⁶ Bradley, D.C., and Thomas, I.M., to be published.